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MULTI-ELEMENTAL ANALYSIS OF CRUDE OILS FROM NIGER DELTA NIGERIA USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Trace elemental analysis using Instrumental Neutron Activation Analysis (INAA) of Crude Oils from seven oil fields in Niger Delta, Nigeria was studied, using Ghana Research Reactor (GHARR-1) operating at 15kW at a thermal flux of 5 $x10^{11}$ $ncm^{-2}s^{-1}$. From the results nine trace elements were identified: Al, Br, Ca, Cl, K, Mg, Mn, Na, and V. This study and previous ones have shown that crude oils from Nigeria are lower in metal content compare to other crude oils elsewhere around the globe. The concentration ranges of the trace elements varied significantly ($P<0.05$) from field to field.

KEYWORDS: INAA, Crude Oils, Nigeria

INTRODUCTION

The origin of trace element in petroleum is highly correlated with the origin of petroleum itself. The origin of petroleum is complex to interpret than that of most rocks. Two different models have been put forward to explain the origin of petroleum. They are: biogenic and abiogenic models respectively (Tissot and Welte 1984, Lewan 1997). Although the biogenic organic model have been widely accepted by the petroleum industry.

The presence of trace elements like; V and Fe in crude oils, bitumen, Coal and shales was first reported by Triebs (1935). The study of trace metals in petroleum have been widely reported in literature (Ball et al, 1960, Filby and Shaty 1975, Valkovic 1978, Ellrich et al., 1985). (Trace elements in Nigeria crude oils were reported by earlier workers (Ndiokwere 1983, Oluwole et al., 1993, Adeyemo et al., 2004, Akinlua 2007 and Muhammad et al., 2003, Kpeglo et al 2015). The analysis of trace element in crude oils and its knowledge provides useful information such as: Characterization of solids and water associated with crude oils, study of heavy oils, understanding fluid interaction in sedimentary basin. Also during refining process: Control of gasoline and deposits in refineries, and process plant, control and quantification of contaminants. Many analytical techniques have been used to determine trace elements in crude oils including, Atomic Absorption spectrometry (Duyck et al; 2007), inductively-coupled plasma Atomic Emission spectroscopy (Al-swaiden, 1996) x-ray florescence (Alvarez et al 1990), neutron activation analysis (Oluwole et al 1993, Adeyemo et al, 2004, Appending et al, 2012) liquid chromatography (Khuhawar et al, 1998) and high performance liquid chromatography (Muhammed et al; 2003) INAA was used as analytical technique to study the trace element distribution in the crude oil samples because of its numerous advantage over other methods which include : very low detection limit for 30-40 elements

(parts per million or parts per billion), significant matrix indepence, possibility to overcome interference in complex gamma-ray spectra (radiochemical separation) and inherent capability for high level of accuracy compared to other trace elemental analysis method (I A E A,1987).

This work aimed at using nuclear analytical technique (INAA) to determining the concentration of trace metals in some crude oils from Niger Delta, Nigeria and to compare their element concentration with those reported in literatures by earlier workers in Nigeria and elsewhere around the world.

MATERIALS AND METHODS

Samples Collection Sites

Seven crude oil samples were collected from onshore well heads within the Niger Delta basin lat. 5.233732 and long. 6.25091 In Nigeria. The map, stratigraphy and sediment logy of Niger Delta basin was reported by Reijers (2011).

Sample Preparation

The crude oil samples were collected in clean plastic bottles (1 liter bottle). Samples were prepared by weighing 200mg on polyethylene films. They were then wrapped with the samples identifies on them. Samples were then parked into polyethylene capsule of diameter 1.60cm (rabbit capsule) and heat sealed. Standards reference material orchard leaves 1571 from the National Institute of Standards and Technology (NIST) were equally weighed as test samples.

Sample Irradiation and Counting

Samples and controls were irradiated in the Ghana Research Reactor (GHARR-1) at the Ghana Atomic Energy Commission, operating at 15kW at a thermal flux of 5 x 10^{11} $n.cm^{-2}.s^{-1}$ Samples were transferred into irradiation sites via pneumatic transfer system at a pressure of 0.60Mpa. The irradiation was categorized according to the half-life of the element of interest as shown in the irradiation scheme in table1.

Table 1: Irradiation Schemes Short Lived Radionuclide's

Element	Target Isotope	Reaction	Product Nuclide	Half Life($t^1/_2$)	Gamma Ray Energies (KeV)	Irradiation Time (S)	Counting Time (S)
Al	^{27}Al	^{27}Al (n, ɣ)	^{28}Al	2.24min	1778.9		
Ca	^{48}Ca	^{48}Ca (n, ɣ)	^{49}Ca	8.7min	3084.4		
Cl	^{37}Cl	^{37}Cl (n, ɣ)	^{38}Cl	37.3min	1642.4, 2167.5	120	600
Mg	^{26}Mg	^{26}Mg (n, ɣ)	^{27}Mg	9.46min	843.8, 1014.4		
Mn	^{55}Mn	^{55}Mn (n, ɣ)	^{56}Mn	2.58h	846.7, 1810.7 2112		
V	^{51}V	^{51}V (n, ɣ)	^{52}V	3.76min	1431.1		
Medium Lived Radionuclide's							
Br	^{81}Br	^{81}Br (n,ɣ)	^{82}Br	35.3h	554.3 776.5		
K	^{41}K	^{41}K (n,ɣ)	^{42}K	12.36h	1524.7	300	600
Na	^{23}Na	^{23}Na (n,ɣ)	^{24}Na	15.02h	1368.6 2654.1		

After the irradiation radioactivity measurement of induced radionuclide was performed by a PC-based gamma-ray spectrometry set-up. It consists of an n-type HPGe detector coupled to a computer based multi-channel analyzer (MCA) via electronic modules. The relative efficiency of detector is 25% and its energy resolution of 1.8keV at gamma-ray energy

of 1332 keV of 60Co. Through appropriate choice of cooling-time, detector's dead time was controlled to be less than 10% identification of gamma-ray product radionuclide was identified through the energies and quantitative analysis of the concentration was by converting the counts as area under the photo peak by the comparator method (Landsberger 1991). Both analyses were done using the gamma-ray spectrum analysis software, ORTC MEASTRO-32. For windows model A65-B32 version 6.05 UMCBI kernel version 6.06 connections-32 version 6.06 Validation of the technique for the experimental set up was done by irradiating a standard reference material (Orchard leaves 1571) for the period of time as the sample in the same location within the reactor. The analysis of the standard reference material in table 2 shows good agreement of measured values with the certified ones. The standard specifications for Bonny light crude oil was shown in table 3.

Determination of Elements Concentration in the Samples

The calculation of trace elements concentrations in the samples was carried out by the comparator method using the same geometry, equal weights of both sample and standard with the same irradiation, decay and counting times, the concentration of the elements in the samples was determined by the expression below. (Ehmann and Diane 1991)

$$C_{sample} = C_{std} \left[\frac{A_{sample}}{A_{std}} \right]$$

Where:

C_{sample} = Unknown concentration of the element in the sample

C_{std} = Known concentration of the element in the standard

A_{sample} = Activity of the sample

A_{std} = Activity of the standard

Table 2: Irradiation of Standard Reference Material 1571 Orchard Leaves Used for Validation

Element	No. of Radiation	Reported Values $Mgkg^{-1}$	This Work $Mgkg^{-1}$
Al	3	Not Reported	12
Br	3	10	12
Ca	3	2.09	2.11
Cl	3	700	698
K	3	1.447wt%	1.40wt%
Mg	3	0.62wt%	0.64wt%
Mn	3	91	91
Na	3	82	81
V	3	Not Reported	37

Table 3: Specification for Nigerian Bonny Light Crude Oil

S/N		
1	Specific gravity @ 60^o /60^oF	0.8387 – 0.8498
2	API @ 15.55^{o}C	35.0 – 37.0 max
3	Density @ 15.55^{o}C	0.85 g/ml max
4	Pour point	< 40^{o}F/4.44^{o}C
5	Sulphur content % Wt	0.14 max

6	Color	Dark brown
7	Kinematic viscosity @ 40^o	3.5 cst
8	Acid number	0.39 max
9	Reid vapour pressure (RVP)	6.52psi max
10	Water and sediment	11% max
11	Iron wt, ppm	1.00 max
12	Nickel wt, ppm	4.00 max
13	Vanadium wt, ppm	2.00 max

Expectation Derivatives From One Barrels	
Products	**Gallons Per Barrels**
Gasoline	19.5
Distillate fuel oil	9.2
Kerosene- type (jet fuel)	4.1
Residual fuel oil	2.3
Liquefied refined gases	1.9
Still gas	1.9
Coke	1.8
Asphat and road oil	1.3
Petrochemical feed stocks	1.2
Lubricants	0.5
Kerosene	0.2
Others	0.3

(Source: Petroleum Analysis Laboratory, PTI Effurun)

Table 4: Trace Elements Concentrations (μgg^{-1}) in Some Crude Oil Samples from Niger Delta, Nigeria

Sample (ID)	Al	Br	Ca	Cl	K	Mg	Mn	Na	V
W1	5.9 ± 0.9	9.0 ± 1.3	775.0±116.3	1431.0± 214.6	14.2± 2.1	53.0 ± 8.0	9.3 ± 1.4	675.2±101.3	2.7 ± 0.4
W2	15.0 ± 2.2	9.4 ± 1.4	222.0 ± 33.2	165.4 ± 24.8	236.8± 35.5	143.0 ±21.5	15.0 ± 2.2	604.9 ± 90.7	0.20 ± 0.03
W3	9.3 ± 1.4	4.0 ± 0.6	654.7 ± 98.2	209.6 ± 31.4	341.5 ± 51.2	167.0 ± 25.1	24.5 ± 3.7	146.0 ± 22.0	1.3 ± 0.2
W4	68.9± 10.3	5.0 ± 0.7	123.6 ± 18.5	277.1 ± 41.6	4321.0 ±648.2	117.0 ± 17.6	12.9 ± 1.9	138.3 ± 20.8	1.5 ± 0.2
W5	45.3± 6.8	6.0 ± 0.9	90.8 ± 13.6	494.3 ± 0.9	2543.2 ± 381.5	88.0 ± 13.0	11.0 ± 1.7	223.9 ± 33.6	2.2 ± 0.3
W6	66.0± 10.0	54.4 ±8.1	669.0 ± 10.3	797 ± 119.6	8.6 ± 1.3	85.0 ± 12.8	8.7 ± 1.3	86.0 ± 13.0	0.8 ± 0.1
W7	84.0± 12.6	107.5±16.5	209.9 ± 31.5	7.3 ± 1.1	134.0 ± 20.0	134.0 ± 20.0	14.7 ± 2.2	96.8 ± 14.5	1.1 ± 0.2

Note: Data behind ± are standard deviations.

Table 5: Pearson Correlation for the Trace Elements

	AL	Br	Ca	Cl	K	Mg	Mn	Na	V
AL	1								
Br	0.571	1							
Ca	-0.805	-0.445	1						
Cl	-0.307	0.163	0.487	1					
K	0.326	-0.446	-0.373	-0.293	1				
Mg	-0.023	-0.210	-0.068	-0.878	-0.043	1			
Mn	-0.328	-0.404	0.350	-0.613	-0.122	0.881	1		
Na	-0.728	-0.407	0.525	0.477	-0.288	-0.319	-0.214	1	
V	-0.203	-0.384	0.462	0.645	0.252	-0.648	-0.293	0.198	1

Table 6: Comparison of Trace Elements Reported in this Work with Other Workers around the Globe

Trace Elements	USA[a]	Libya[a]	Venezula[a]	Canada[a]	Middle East[b]	China[c]	Ghana[d]	Nigeria Present Work
Al	0.30	-	1.0	-	7.0	46.4	2.96	5.9-84.0
Br	0.29	1.33	-	0.491	-	19.6	1.67	4.0-107.5
Ca	1.6	-	-	-	-	-	0.31	90.8-775.0
Cl	1.47	1.81	-	39.3	-	1000	12.95	7.3-1431.0
K	2.5	4.93	2.1	-	0.7	-	0.09	8.6-4321
Mg	2.0	-	1.7	-	7.0	-	1.32	53.0-143.0
Mn	1.2	0.79	0.21	0.048	-	5.89	0.28	8.7-24.5
Na	13.2	19.0	20.3	3.62	0.5	891	110	86.0-675.2
V	7.5	8.2	11.10	13.6	100	10.4	0.40	0.2-2.7

a Filby and Shan 1975 and Hitchon et al 1975

b Williams and Cawley 1963

c Chifang et al 1991

d Kpeglo et al 2015

Table 7: Comparison of Vanadium Concentrations in Nigerian Crude Oils Reported by this Work and Other Workers

Element	Concentration	Unit	Source
V	11.2-29.2	μgg^{-1}	Akinlua et al., 2007
	0.009-1.832	μgg^{-1}	Nwachukwu et al., 1995
	3.70- 40.0	μgg^{-1}	Udo et al., 1992
	0.54-1.195	μgg^{-1}	Oluwole et al., 1993
	0.642-0.10	μgg^{-1}	Ndiokwere, 1983
	22.5-1060	ngg^{-1}	Muhammad et al., 2013
	14000-99000	ngg^{-1}	Olajire and Oderinde 1995
	1.95-7.94	μgg^{-1}	Kpeglo et al., 2015
	0.2-2.7	μgg^{-1}	Present Work

RESULTS AND DISCUSSIONS

INAA technique was used to analyze short –lived and medium-lived trace elements in crude oils from seven oil fields in Niger Delta Nigeria, nine trace elements: Al, Br, Ca, Cl, K, Mg, Mn, Na and V were analyzed and Shown in table 4. From the data it can be observed that the trace elemental concentration of the crude oils varied appreciably due to variation of geographical location of the oil fields. The nature of these trace elements and their relative abundance in crude oils can provide information about the origin, migration and maturation of petroleum as well as indicating the regional geochemical prospecting base (Chifang et al., 1991, Oluwole et al., 1993, Elirich et al., 1985).

Transition elements like Mn and V in the crude oil samples could be used to explain the origin of the crude oils from the decomposition of marine living organisms (Appenteng et al, 2012). Also their ability to form complex or chelate in a σ and π bonding form with some organic compounds (Herberhold 1972). The relativity higher concentration of elements like; Ca (90 - 775) $\mu gg^{-1,}$ Cl (210 - 1431) μgg^{-1}, Na (86 - 675) μgg^{-1} in the crude oil samples suggest that the source of the crude oils from sedimentary deposition in the sea.

Table 5 is the pearson correlation computed for the trace elements. It was observed that some elements showed some significantly positive correlation with each other. Br – Al (0.6), Cl – Ca (0.5), Mn – Mg (0.9), Na –Ca (0.5), Na – K (0.5), V – Ca (0.5) and V – Cl (0.6). Table 6 showed the comparison of trace elements reported in this work with other workers around the globe. The trace elements content in the crude oils of Niger Delta Nigeria was higher than those from USA and Canada reported by Filby and Shan 1975, Hitchon et al 1975. But Vanadium content in Nigerian crude oils was very low compared to the values reported by other workers. In table 7 the Vanadium in Nigerian crude oils were compared with reported values by previous workers on Nigerian crude oils. Our values were in agreement with those reported by Nwachukwu et al 1975, Oluwole et al 1993 and Kpeglo et al., 2015.

CONCLUSIONS

The (INAA) result of this study has shown that the trace element content of Nigerian crude oils is lower compared to others reported around the globe. Relatively lower concentrations of the crude oils in V and Br is indication of good quality crude oils with minimal refining process and negative environmental impacts. Good positive correlation between Ca, Cl and Na suggest marine organic origin and sea salt component.

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